

Model Pseudopotentials and Dynamical Properties of Simple Metals

S. K. Srivastava

Physics Department, Allahabad University, Allahabad-211002, India.

Abstract

The pseudopotential investigation of the dynamical properties of simple metals is discussed, and various model pseudopotentials are used to determine the thermal resistivity as a function of temperature at constant volume for the b.c.c. metals Li, Na, K, Rb, and Cs and the f.c.c. metals Cu, Ag, and Au. Krebs's (1965) lattice dynamical model is used to supply dynamical structure factors. The resulting theoretical thermal resistivities are compared with available experimental values.

1. Introduction

Considerable progress has been made both in experimental and theoretical studies of the electrical resistivity of metals (Bardeen 1937; Berman and MacDonald 1951, 1952; Baily 1960; Dugdale and Guban 1962; Dugdale and Phillips 1965; Singh and Sharma 1969*a*; Srivastava 1973). However, very little work has been reported on the thermal resistivity of metals (White 1953*a*, 1953*b*; MacDonald *et al.* 1956; Singh and Sharma 1969*b*; Ekin 1972; Laubitz and Cook 1972). These authors used the pseudopotential formalism with lattice mechanics to investigate the temperature dependence of the thermal resistivity of simple metals. In such calculations it is essential to have a knowledge of the phonon frequencies and the polarization vectors besides the pseudopotential form factors. The real advantage of this approach is that the Umklapp processes and coupling to transverse phonons enter in the problem directly. In this method, information about the ion positions is gathered through the dynamical structure factor $S(\mathbf{q}, \omega)$ while electron-ion scattering is considered through the pseudopotential form factors $U(\mathbf{q})$.

Van Hove (1954) showed that $S(\mathbf{q}, \omega)$ can be obtained directly from inelastic scattering experiments. However, this factor has not been measured in sufficient detail to be of use for the calculations of the present paper. Since in the one-phonon approximation, $S(\mathbf{q}, \omega)$ is directly related to the phonon spectrum, a force constant model has been used in this paper for the evaluation of dynamical structure factors.

The calculation of the $U(\mathbf{q})$ is quite complex in practice, it being very difficult to calculate them from first principles. Consequently, the electron-ion potential is generally presented in the form of a model which contains certain open parameters. Many such pseudopotential models have been developed; e.g. recently the theory of pseudopotential spherical functions (Srivastava 1974*a*, 1974*b*) has been used in the description of one-parameter model pseudopotentials (Ashcroft 1966, 1968; Srivastava and Sharma 1970).

In the present paper a theoretical calculation is given for the thermal resistivity at constant volume of certain simple b.c.c. and f.c.c. metals. The Krebs (1965) lattice dynamical model has been used for the evaluation of the dynamical structure factor $S(\mathbf{q}, \omega)$. This model is superior to others, such as those of Bhatia and Horton (1955), de Launay (1956) and Sharma and Joshi (1963, 1964), in the sense that the frequencies given by it are periodic in the reciprocal space and satisfy the symmetry requirement of the lattice. Various pseudopotential models (Animalu and Heine 1965; Ashcroft 1966, 1968; Schneider and Stoll 1966; Shaw 1968; Srivastava and Sharma 1970) are employed in the calculation besides the two proposed model pseudopotentials described in Section 2 below. In another study, these model potentials have presented satisfactory results for various properties of simple metals (Srivastava 1975). In Section 3, the theory of the present calculations is described and the results obtained are discussed in Section 4.

2. Model Pseudopotentials

On denoting the ion-core repulsive potential by $Ze^2r^{-1}F_l(r)$, the potential is made l dependent (l being the angular quantum number). This yields an ion-core potential matrix element of the form

$$\begin{aligned} \langle \mathbf{k} + \mathbf{q} | V_b(\mathbf{q}) | \mathbf{k} \rangle = & - \int Ze^2r^{-1} \exp(i|\mathbf{k}' - \mathbf{k}|r) d^3r \\ & + \int_{r < r_c} Ze^2r^{-1} F_l(r) \exp(i|\mathbf{k}' - \mathbf{k}|r) d^3r, \end{aligned} \quad (1)$$

where $F_l(r)$ is a normalized function which is related to the Fourier transform of the core electron density $n_l(q)$ through the newly defined pseudopotential spherical function $s_l(x)$ for $x = qr_c$ as follows:

$$\int_{r < r_c} F_l(r) \sin(qr) dr = q^{-1} \sum_{l'=0}^l s_{l'}(qr_c) = (qN)^{-1} \sum_{l'=0}^l n_{l'}(q). \quad (2)$$

Here N is the electron number density and the function $s_{l'}(qr)$ is given by

$$\sum_{l'=0}^l s_{l'}(qr) = q^2r \sum_{l'=0}^l \int (-1)^{-l'+2} (qr)^{-l'+1} j_{l'}(qr) dr, \quad (3)$$

where $j_{l'}(qr)$ is a spherical Bessel function. From equations (2) and (3), the value of $F_l(r)$ becomes

$$F_l(r) = \text{cosec}(qr) \sum_{l'=0}^l (-1)^{l'+1} \{ -(q'r)^{-l'+2} j_{l'}(q'r) + (q'r)^{-l'+1} j_{l'-1}(q'r) \}. \quad (4)$$

Case 1

For $l = 1$, equation (1) produces under a pseudopotential local approximation

$$\langle \mathbf{k} + \mathbf{q} | V_b(\mathbf{q}) | \mathbf{k} \rangle = \frac{4\pi Ze^2}{\Omega} r^2 \sum_{l'=0}^1 (-1)^{-l'+2} \int (qr)^{-l'+1} j_{l'}(q'r) dr - \frac{4\pi Ze^2}{\Omega q^2},$$

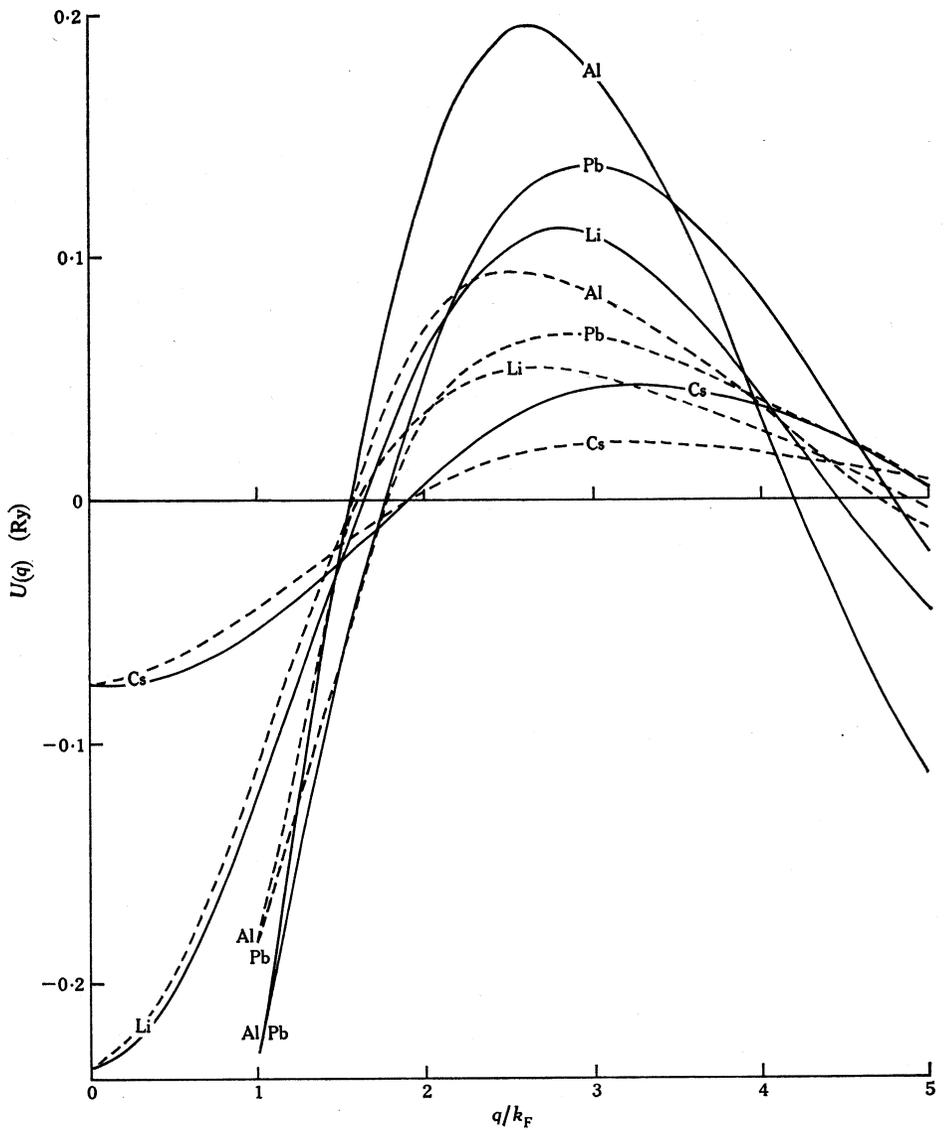


Fig. 1. Comparison of pseudopotential form factors U (Rydberg units) for the indicated metals as functions of the momentum transfer vector q expressed in units of the Fermi momentum k_F . Full curves denote results of the model of Srivastava and Sharma (1970) and dashed curves those of Ashcroft (1966, 1968).

since $F_1(r) = q'r$. For $q' \rightarrow q$, this gives

$$\langle k+q | V_b(q) | k \rangle = -4\pi Ze^2 / \Omega q^2 + \beta, \quad \text{with} \quad \beta = (4\pi Ze^2 / \Omega q^2) \sum_{l'=0}^1 s_{l'}(qr_c), \quad (5)$$

which is the model potential described by Srivastava and Sharma (1970).

Case 2

For $l = 0$, under the limiting condition $(q'r) \rightarrow 0$, equation (1) produces

$$\langle \mathbf{k} + \mathbf{q} | V_b(q) | \mathbf{k} \rangle = -(4\pi Ze^2 / \Omega q^2) \cos(qr_c), \quad (6)$$

since $F_0(r) = 1$, which is the model potential described by Ashcroft (1966, 1968).

A comparison of form factors for Al, Pb, Li and Cs as derived for these two cases is shown in Fig. 1. It can be seen that the form factors of the Srivastava-Sharma (1970) model (full curves) do not converge rapidly at higher values of the modulus of the momentum transfer vector q . This presents a difficulty in problems in which summation is required for higher values of q . This deficiency can be overcome by incorporating the discussions of Austin *et al.* (1962) and Harrison (1963) into the leading term $\langle \mathbf{k} + \mathbf{q} | \alpha \rangle$ for the core function in the s state, which varies as $A \exp(-r/r_c)$ and may be described by

$$\langle \mathbf{k} + \mathbf{q} | \alpha \rangle = \int_{r < r_c} A \exp(-r/r_c) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3r. \quad (7)$$

Here α is a representation for the eigenstate, which transforms to the above potential in the form

$$V_b(q) = [-4\pi Ze^2 q^{-2} + \beta \{1 + (qr_c)^2\}^{-2}] \Omega^{-1}. \quad (8)$$

In accordance with the arguments of Austin *et al.* and Harrison, two suitable model potentials are proposed:

Model I

$$V_b(q) = -4\pi Ze^2 q^{-2} + \beta [\gamma + \{1 + (qr_c)^2\}^2] / [1 + \{qr_c\}^2]^2 \Omega^{-1}, \quad (9)$$

where

$$\gamma = 1 - \sum_{l'=0}^1 s_{l'}(qr_c); \quad (10)$$

Model II

$$V_b(q) = [-4\pi Ze^2 q^{-2} + \beta \{\gamma - 1 + \exp(-\frac{1}{3}\gamma')\} / \gamma'] \Omega^{-1}, \quad (11)$$

where

$$\gamma' = \frac{1}{3}(qr_c)^3 \{1 + (qr_c)^2\}^2. \quad (12)$$

We have taken into account the cancellation effect in the core region from the Wigner-Seitz function. As for other one-parameter models, the limiting value of $V_b(q)$ as q goes to zero is $-4\pi Ze^2 q^{-2} \Omega^{-1}$ for both models, and this correctly satisfies the limit required by charge neutrality. In addition, the condition $qr_c = \frac{1}{2}\pi$ is satisfied for the cutoff region of the potentials, and this condition is used here to determine the ionic radius r_c for various simple metals. This is done by matching the first node of $V_b(q)$ with the bare-ion-model potential form factors (without the orthogonality correction) of Heine and coworkers (Heine and Abarenkov 1964; Abarenkov and Heine 1965; Animalu and Heine 1965). This node usually lies in the range $1.4 < q/k_F < 2$. The Heine-Abarenkov model is preferred here for the reason that it gives a satisfactory description of the transport properties of several simple metals. For the noble metals, the form factors of Moriarty's (1970) model potential

have been used. The resulting values of r_c (atomic units) for 10 simple metals are:

Li	Na	K	Rb	Cs	Cu	Ag	Au	Al	Pb
1.678	1.758	2.133	2.256	2.425	1.221	1.436	1.424	1.131	1.069

For screening the potential, the static Hartree dielectric constant has been used.

3. Theory

The variational calculation for the ideal thermal resistivity gives (Ziman 1960; Singh and Sharma 1969*a*, 1969*b*)

$$\rho = k_B^{-1} \iiint \left(|\phi_k - \phi_{k'}|^2 P(\mathbf{k}\mathbf{q}, \mathbf{k}') d\mathbf{k} d\mathbf{k}' d\mathbf{q} \right) / \left| \int (E_k - E_F) \mathcal{V}_k \phi_k \frac{\partial f_k^0}{\partial E_k} d\mathbf{k} \right|^2, \quad (13)$$

where P is the scattering operator, f_k^0 is the equilibrium distribution function, and ϕ is the trial function, which for elastic scattering is considered to be

$$\phi_k = (E_k - E_F) \mathbf{k} \cdot \mathbf{u}, \quad (14)$$

with \mathbf{u} being a unit vector parallel to the heat current. For simple metals, equation (13) takes the form

$$\rho = \left(\frac{2}{9} L_0 T \hbar e^2 k_F^2 s^2 \right)^{-1} \iiint \frac{ds}{v_k} \frac{ds'}{v_{k'}} \left(\frac{1}{3} q^2 + (k_F^2 - \frac{1}{6} q^2) \pi^{-1} (\beta \omega_{q,p})^2 \right) \times |\langle \mathbf{k}' | U | \mathbf{k} \rangle|^2 \beta \omega \{1 - \exp(-\beta \omega)\}^{-1} S(\mathbf{q}, \omega) d\omega \quad (15)$$

in the weak scattering approximation. Here $\langle \mathbf{k}' | U | \mathbf{k} \rangle$ is the matrix element of the pseudopotential, $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ is the momentum transfer vector, v_k is the electron velocity in the state $|\mathbf{k}\rangle$, s is the area of the Fermi surface, p is the polarization index, L_0 is given by $\frac{1}{3} \pi^2 (k_B/e)^2$ and β is given by $\hbar/k_B T$, where k_B is Boltzmann's constant and T the temperature. The surface integrals are taken over the Fermi surface. The quantity $S(\mathbf{q}, \omega)$ is the Fourier transform of the space-time dependent correlation function, which according to Van Hove (1954) can be expressed as

$$S(\mathbf{q}, \omega) = (2\pi N)^{-1} \int \exp(i\omega t) dt \left\langle \sum_{i,j} \exp(-i\mathbf{q} \cdot \mathbf{R}_i(t)) \exp(i\mathbf{q} \cdot \mathbf{R}_j(0)) \right\rangle T, \quad (16)$$

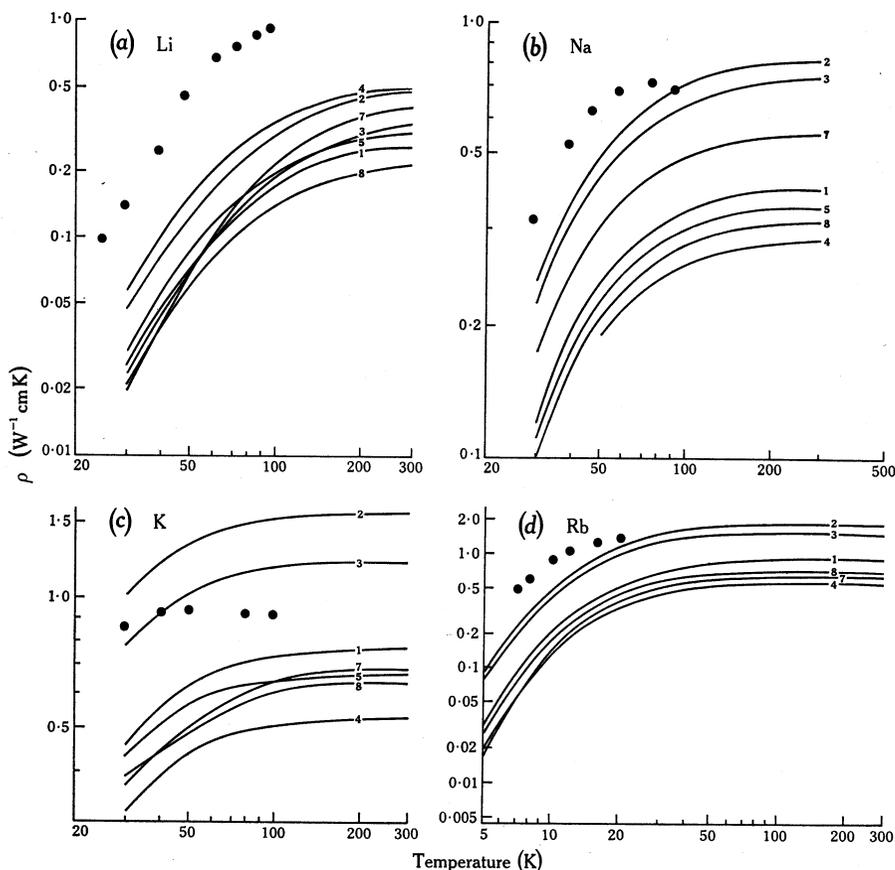
where $\mathbf{R}_i(t)$ and $\mathbf{R}_j(0)$ are position vectors of the i th and j th ions at times t and 0 respectively, N is the number of ions, the angle brackets denote the thermal average at temperature T , and the summation is taken over all ions in the lattice. The ion position $\mathbf{R}_i(t)$ can be expressed by the relation

$$\mathbf{R}_i(t) = \mathbf{R}_i(0) + \mathbf{U}_i(t), \quad (17)$$

where the first term represents the equilibrium value and the second is the displacement given by

$$\mathbf{U}_i(t) = (MN)^{-\frac{1}{2}} \sum_{\mathbf{q},p} \mathbf{e}_{\mathbf{q},p} \exp(i\mathbf{q} \cdot \mathbf{R}_i(0)) (2\omega_{\mathbf{q},p})^{-\frac{1}{2}} \{a_{\mathbf{q},p}^+(t) + a_{-\mathbf{q},p}(t)\}. \quad (18)$$

Here M is the ion mass, $a_{q,p}^+(t)$ and $a_{-q,p}(t)$ are creation and annihilation operators respectively, and $e_{q,p}$ is the polarization vector. The linear terms in the displacement do not appear because they are proportional to the phonon creation and annihilation operators, so that they average out to zero.



Figs 2a-2h. Comparison of theoretical and experimental results for the thermal resistivity ρ as a function of temperature for the indicated metals. The theoretical models are denoted as follows: 1, model I; 2, model II; 3, Srivastava and Sharma (1970); 4, Animalu and Heine (1965); 5, Ashcroft (1966, 1968); 6, Moriarty (1970); 7, Schneider and Stoll (1966); 8, Shaw (1968). The sources of the experimental data are listed in Table 2.

Using the harmonic approximation and the assumption that the phonons are in thermal equilibrium, and after performing integrations over the grand canonical ensemble and time, we can convert the expression for $S(\mathbf{q}, \omega)$ into

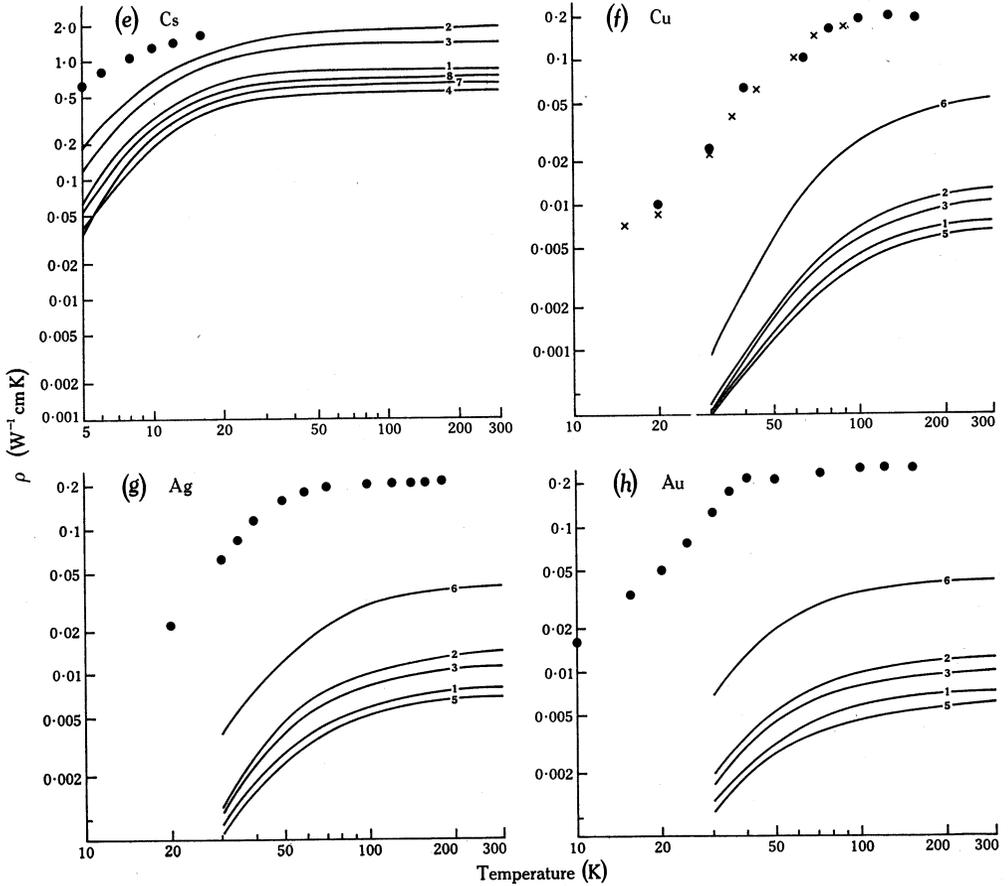
$$S(\mathbf{q}, \omega) = \frac{\hbar}{2M} \sum_p \frac{(\mathbf{e}_{q,p} \cdot \mathbf{q})^2}{\omega_{q,p} \{ \exp(\beta \omega_{q,p}) - 1 \}} \left(\delta(\omega - \omega_{q,p}) + \exp(\omega_{q,p}) \delta(\omega + \omega_{q,p}) \right). \quad (19)$$

By putting

$$\int_{-\infty}^{\infty} [S(\mathbf{q}, \omega) \beta \omega \{ 1 - \exp(-\beta \omega) \}] d\omega = S(\mathbf{q}) \quad (20)$$

and inserting equation (19) into equation (20), we get

$$S(\mathbf{q}) = \frac{\hbar^2}{Mk_B T} \sum_p \frac{(e_{q,p} \cdot \mathbf{q})^2}{\{\exp(\beta\omega_{q,p}) - 1\} \{1 - \exp(-\beta\omega_{q,p})\}} \quad (21)$$



Figs 2e-2h.

On a free-electron model for the conduction band, the two surface integrals in equation (15) can be converted into a three-dimensional integral over q . Thus, the final expression for the thermal resistivity becomes

$$\rho = \left(\frac{1}{9} L_0 T n e^2 \hbar v_F^2 k_F^4\right)^{-1} \int S(\mathbf{q}) U^2(\mathbf{q}) q^{-1} \left\{ \frac{1}{3} q^2 + (k_F^2 - \frac{1}{6} q^2) (\beta \omega_{q,p})^2 \pi^{-2} \right\} d^3 q. \quad (22)$$

4. Results and Discussion

The ideal thermal resistivities for the b.c.c. metals Li, Na, K, Rb and Cs and for the f.c.c. metals Cu, Ag and Au as functions of temperature have been computed from equation (22). The function $S(\mathbf{q})$ was obtained from equation (21) using the Krebs (1965) lattice dynamical model for the phonon frequencies and the polarization vectors. The following models have been used to calculate $U(\mathbf{q})$: models I

and II of Section 2; the other one-parameter model potentials (Ashcroft 1966, 1968; Srivastava and Sharma 1970); the Schneider and Stoll (1966) model; the Animalu and Heine (1965) model; the optimized model potential of Shaw (1968); and Moriarty's (1970) model. The modified Houston spherical six-term integration procedure as developed by Betts *et al.* (1956) has been used in the angular integration of equation (22). The six directions used for q were (100), (110), (111), (210), (211) and (221). The elastic constants and the lattice constant used are given in Table 1.

Table 1. Physical constants for metals

Metal	Elastic constants (10^{10} Pa*)			Reference	Semilattice constant (10^{-8} cm)	Temp- erature (K)
	c_{11}	c_{12}	c_{44}			
Lithium	1.481	1.248	1.077	Nash and Smith (1959)	1.746	78
Sodium	0.741	0.624	0.419	Daniels (1960)	2.145	300
Potassium	0.372	0.315	0.188	Smith and Smith (1966)	2.672	295
Rubidium	0.296	0.244	0.160	Roberts and Meister (1966)	2.850	80
Caesium	0.245	0.208	0.159	Huntington (1958)	2.023	0
Copper	16.839	12.142	7.539	Kittel (1971)	1.808	300
Silver	12.399	9.367	4.612	Kittel (1971)	2.040	300
Gold	19.234	16.314	4.195	Kittel (1971)	2.035	300

* Note that 1 Pa (pascal) \equiv 10 dyn cm $^{-2}$.

Table 2. Ranges of experimental thermal resistivity values

Metal	Temperature range (K)	Reference
Lithium	24.6–95.4	MacDonald <i>et al.</i> (1956)
Sodium	24.6–94.4	Berman and MacDonald (1951)
Potassium	2.0–100	MacDonald <i>et al.</i> (1956)
Rubidium	6.8–20	MacDonald <i>et al.</i> (1956)
Caesium	5–16	MacDonald <i>et al.</i> (1956)
Copper	15–90	Berman and MacDonald (1952)
	20–160	White (1953a)
Silver	20–160	White (1953b)
Gold	10–150	White (1953b)

The computed values of the thermal resistivities of the selected b.c.c. and f.c.c. metals are plotted in Figs 2a–2h and compared with available experimental values. The ranges in temperature over which experimental values of the thermal resistivity are available are listed in Table 2. An overall perusal of Figs 2a–2h indicates that the general shape of the theoretical and experimental curves is the same but that, in general, the theoretical curves lie below the experimental values. It can also be seen that the Li curve for the Animalu and Heine (1965) model, the Na, Rb and Cs curves for model II, the K curve for the Srivastava and Sharma (1970) model, and the curves of the noble metals for Moriarty's (1970) model all lie close to the experimental measurements. For potassium, model I (in the high temperature region) and model II (in the low temperature region) provide better results. The deficiency in the theoretical results may arise through the use of the first-order variational

solution of the Boltzmann equation. The observed discrepancies between the theoretical and experimental values of the resistivities at higher temperatures may be attributable to the neglect of various anharmonic effects, such as multiphonon processes, the Debye-Waller factor, and changes of the elastic constants with temperature, etc. They may be partly due to the small change in the pseudopotential caused by volume changes through thermal expansion. It is noticeable that Li and Na undergo the martensitic transformation below 75 K and 40 K respectively, and this might in part account for the discrepancy found in the case of these metals at low temperatures. The present results also reveal that the thermal resistivity is very sensitive to the form of the pseudopotentials.

Acknowledgments

The author expresses his thanks to Professor Vachaspati, Professor S. K. Joshi, Professor S. K. Sinha and Dr Bal Krishna Agrwal for illuminating discussions and comments, and Dr Hari Prakash and Dr Naresh Chandra for their interest and encouragement. He is grateful to the authorities of the computer centre, I.I.T., Kanpur, for providing their computing facilities. This work is supported by the C.S.I.R., New Delhi.

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Manuscript received 27 November 1974